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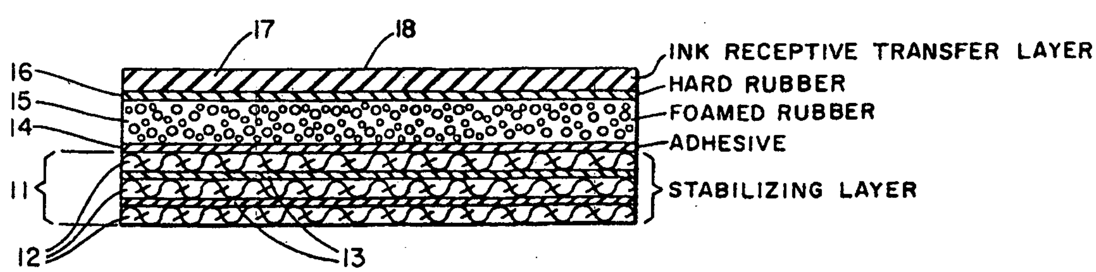
(54) Closed cell foam printing blanket and foaming meth d

(57) A resilient compressible printing element is provided having a base layer of a stabilising material e.g. a fabric laminate 11 and a compressible rubber layer 15 with foamed closed cells therein. The closed cells are formed by the use of blowing agents which are activated and foam the material while, an external pressure is applied to the material to restrict expansion. The stabilising material may be a laminate of three layers of adhesively bonded fabric.

FIG. 1



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Sheet 1

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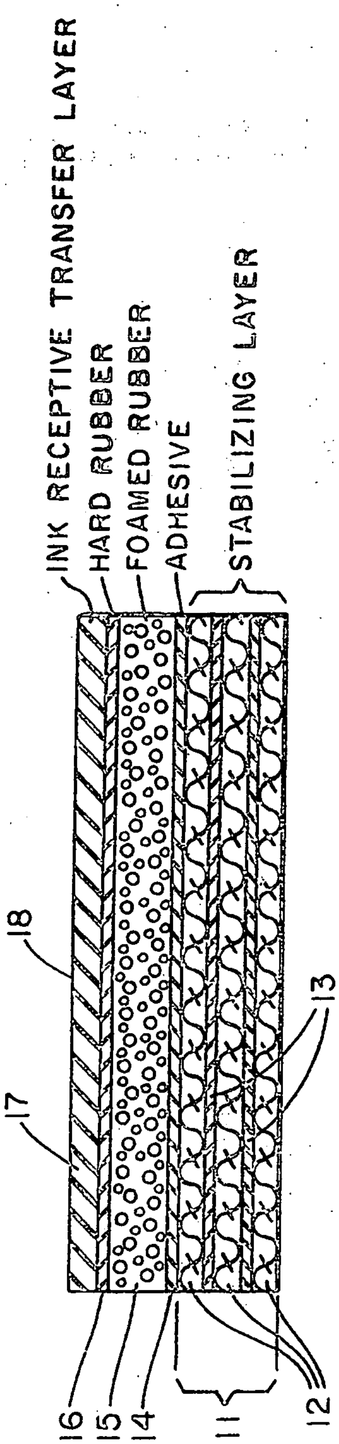
FIG. 1



2056883 2 Sheets
Sheet 2

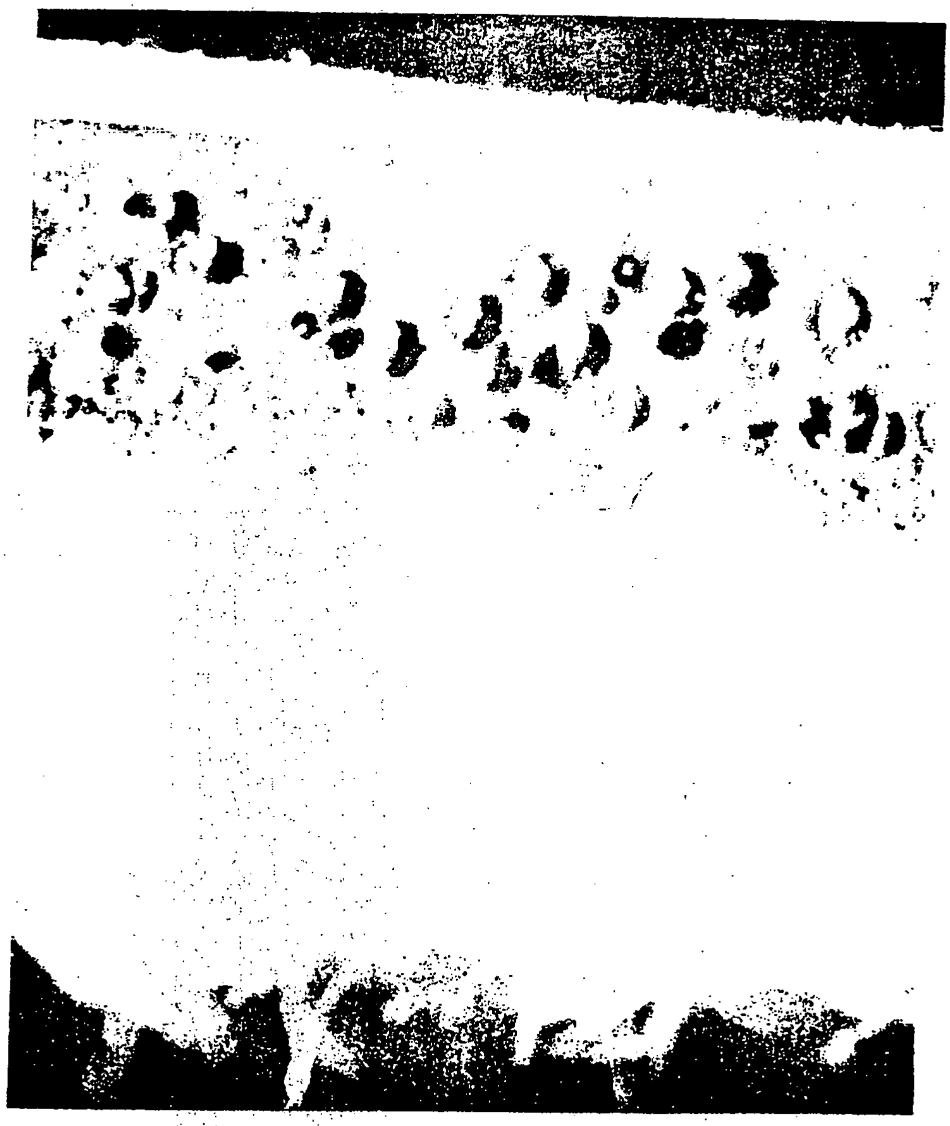


FIG. 2

SPECIFICATION

Closed cell f am printing blanket and foaming method

This invention relates to resilient compressible printing elements and in particular to those having an intermediate layer of foamed rubber and to a method of foaming materials and the foamed materials produced by the method.

It is known in producing resilient compressible printing elements to have a cellular intermediate layer (see "New Developments in Off-Set Blankets" pages 2–7, *Professional Printer*, Volume 22, Number 6). However, the only closed cell materials revealed in the article were those made using microspheres which were crushed. When blowing agents were used an open cell structure was produced in which the cell walls ruptured causing the cells to be interconnected. On page 3 of the article it is pointed out that open celled foams are not satisfactory as compared with the closed cells produced by the breaking of microspheres which yielded good results because the closed structure recovered more quickly than the open structure because the gas contained in the voids was compressed and only had to expand after compression. Among other deficiencies, the use of microspheres, is an expensive manufacturing procedure and results in the retention of a substantial amount of residue within the void from the microsphere body. U.S. Patent 3,887,750 discloses the use of discrete hollow fibres to obtain the closed cells and U.S. Patent 3,795,568 discloses the use of particles of compressible latex foam rubber to obtain the closed cells. Both of these approaches have the disadvantage of having substantial material within the closed cell of the matrix forming the compressive layer. They also require the premanufacture of the structures to be incorporated in the rubber matrix.

According to the present invention, a resilient compressible printing element, typically for use in lithographic printing, is provided having a base layer which is a machine direction, elongation stabilizing material or an adhesive material, and a compressible layer, with the compressible layer being a layer of foamed rubber having a substantially closed cell structure. Preferably at least about 50% of the foamed cells are closed and have average cell diameters of 1/2 to 10 mils (0.125 to 0.25 mm) and the compressible layer has a void volume of at least 20%, a thickness of not more than 30 mils (0.75 mm) or 35 mils (0.875 mm) and is not more than 20 mils (0.5 mm) from the face of the element. An important feature of the invention is being able to form a printing element that is free of any reinforcing fabric between the compressible layer and the face coating. An important aspect in making this possible is believed to be the provision of a hard rubber layer between the compressible layer and the face layer, preferably one having a durometer of 75.

The present invention also provides a process for foaming materials. The process involves incorporating a foaming agent in the material and foaming the material while subjecting the material to an external pressure that yields to the foaming while remaining intact, preferably by applying superatmospheric gas pressure to the outer surface of the material. The material is preferably a plastic rubber when the foaming begins and is a significantly set rubber before the foaming is completed with the external pressure being maintained on the outer surface of the material until the foaming is at least substantially complete. The external pressure maintained on the material during foaming is preferably at least 10 psi (0.7 kg/cm^2) gauge, more preferably 50 to 200 psi (3.5 to 14 kg/cm^2) gauge. Preferably the material incorporating the foaming agent is applied to the stabilizing layer before foaming and after foaming a face layer is applied over the foam opposite the stabilizing layer.

Insofar as is known, in the past, in the usual process when a blowing or foaming procedure was to be carried out every effort was made to reduce external pressure in order to encourage the foam expansion. As far as is known it has never been the practice to deliberately apply external pressure onto a material that was being foamed to control the rupturing of cells and provide the formation of a superior foamed product. (Closed cell foams have been manufactured in pressure moulds where the physical size (volume) of the mould was fixed).

Closed cell systems generally provide sufficient unfoamed rubber surrounding the cells to provide a large enough tensile force to prevent delamination or internal splitting of the compressible foam layer. This property also permits the use of thicker compressible layers to provide ad quate void volume to absorb minor smashes preventing damage to the printing blanket.

A closed celled system also prevents capillary absorption of solvent through the edges of a printing element. Open celled foam and non-woven compr ssible layers are subject to capillary absorption with resulting w akening f the compressibl layer.

The present invention will now be illustrated, merely by way of example, with r ference to the accompanying drawings, in which:

Figure 1 is an enlarged sectional view of a lithographic printing blanket of the present invention.

Figure 2 is a photomicrograph in the same view as the illustrative drawing of Fig. 1.

Referring to Fig. 1 the lithographic printing blanket may be seen to have a stabilizing layer 11 in the form of a laminate comprised of, in this case three, woven e.g. cotton textiles 12 laminated together with adhesive e.g. neoprene layers 13. Next a nitrile rubber adhesive lay r 14 is provided and above this is a compressible foamed layer 15. Above th compressible layer 15 is a hard rubber stabilizing layer 16. The stabilizing layer 16 is overlaid by a face layer 17 whose surface forms an inking face 18.

The principal features of the composite lithographic printing blanket of the present invention are foamed layer 15 and the hard rubber stabilizing layer 16 (if present). The composition of the hard stabilizing rubber layer 16 is not novel; it is its position in combination with the closed celled compression layer 15 which is novel. The stabilizing layer 11 and the face layer 17 may be of any construction and composition known to the art of printing blankets, varied to accommodate the specific intended end use. It is considered important to have, as a general proposition, the compressible foamed layer 15 as close to the outer face 18 of the composite resilient compressible printing element as possible.

It is also considered important to employ the hard rubber layer 16 because this is one of the features that helps to make possible the elimination of the necessity of adding a woven stabilizing layer between the compressible layer and the face layer 17. The use of a fabric between the compressible layer and the face layer was previously necessary to distribute the impact of impingement to prevent the compressible layer from flowing and distorting the print, particularly dots. The fabric also prevented the prior art foams from splitting and otherwise being damaged. The inherent strength of the closed celled foam layer itself is perhaps the more important key to being able to omit the fabric and indeed the hard, rubber layer 16 is not believed to be necessary in all printing blanket applications. While it is a feature of the invention to be able to leave out the fabric reinforcement, in its broader concept, certainly the use of a fabric layer is not excluded.

The stabilizing layer 11 provides low elongation in the machine direction. The stabilizing layer may be omitted in proper circumstance and an adhesive (pressure sensitive) layer applied to adhere the printing blanket to the blanket cylinder. The blanket cylinder then serves as the stabilizer.

In its broadest application the invention may be considered simply the substitution of the foamed layer 15 for the compressible layer in any resilient compressible printing element. This compressible layer is a key element of the present invention and is a layer of foamed rubber having a substantially closed celled structure. The cells of the foamed compressible layer are preferably at least 50%, more preferably at least 80%, closed celled with the cells preferably having an average diameter of 1/2 mil to 10 mils (0.0125 to 0.25 mm), more preferably of 2 to 7 (0.05 to 0.175 mm). The void volume of the compressible layer is preferably at least 20%, more preferably at least 30%, and the thickness is preferably not more than 30 mils (0.75 mm), more preferably not more than 20 mils (0.5 mm), with the foamed compressible layer preferably being not more than 20 mils (0.5 mm), more preferably not more than 15 mils (0.375 mm), from the face 18 of the element.

The foamed layer is generally formed as a virgin blown foam by gas expansion and is free of solid material internal of the closed cell walls of the rubber matrix of the compressible layer other than blowing agent residue. The cells thus do not contain any residue beyond chemical blowing agent residue. This means that no particulate material or structurally significant cell wall linings and the like need be present which can interfere with, or modify, the compression characteristics of the matrix and the inherent properties of its virgin cell structure either initially or over a period of time. By "virgin" is meant that the cellular structure is formed in the structure as it is to be used and not chopped up and bound together with, for example, a binder.

Any rubber having good integrity can be compounded for use as the matrix of the compressible layer in the present invention. In addition to the preferred nitrile rubber, natural neoprene, butadiene-styrene, ethylene-propylene, polybutadiene, polyacrylic polyurethane, epichlorohydrin, chlorosulphonated polyethylene can, for example, be used. The rubber compositions can of course contain stabilizers, pigmenting agents and plasticizers, for exampl . In addition th composition will normally be cross-linked with a peroxide or more oft n a vulcanizing agent, particularly sulphur. Of course, a blowing ag nt is mployed to produc th foam cells. The preferred blowing agents are heat activated bl wing agents such as those decomposing to produce nitrogen gas.

The p rcentage of the cells that are closed can be determined by slicing thr ugh a secti n f the clos d celled structure, then counting the cells that do not exhibit any opening into another cell or void, then counting the open cells and then calculating the p rcent of th total that are closed. The cells are c unted in any selected continu us area so l ng as the area includes at least 100 severed cells pened for inspecti n. To det rmin the cell diamet r of the closed cells, the 20% of the cl sed cells having th largest openings are measured and the av rag of their

The hard rubber layer between the c mpr ssible layer and the fac layer pref rably has a dur met r of at least 75 (Sh re A hardness). Its hardness is pr ferably 75 to 95 durometers. Gen rally such rubbers contain substantial amounts of inorganic filler or carbon black and more rigid thermosetting p lymers such as the phenolic resins in combination with rubbers such as thos listed above for th compressible matrix rubber.

Th process for foaming materials according to the present inventi n involves incorporating a foaming agent in the material and foaming the material while subjecting the material to an external pressure and, subsequently, heat. This is preferably done by applying super-atmospheric gas pressure to the outer surface of the material, activating the foaming agent by thermal energy while maintaining the super-atmospheric gas pressure on the outer surface of the material, and foaming the material through the thermal decomposition of the foaming agent while maintaining the superatmospheric pressure on the outer surface of the material. The material is preferably in a plastic rubber state when the foaming begins and is significantly set or, that is, vulcanized or cross-linked before the foaming is completed, and the super-atmospheric pressure is maintained on the outer surface of the material until the foaming is at least substantially complete.

The external gas is preferably air and the pressure is preferably at least 10 psi (0.7 kg/cm^2) gauge, more preferably 50 psi (3.5 kg/cm^2) and most preferably at least 100 psi (7 kg/cm^2). Preferably the external pressure is 50 to 200 psi (3.5 to 14 kg/cm^2) gauge. (All psi's are gauge readings above atmospheric). External pressure may in some instances be applied by other means than gas, for example by a tensioned belt.

The preferred materials to be foamed are those mentioned above for the composition of the foamed material. These, when properly compounded, yield set rubber matrices. Preferably the procedure for manufacturing the foamed structure provides for heating to both activate the foaming agent and stabilize the foam, in the case of rubber by vulcanization or cross-linking.

To prepare the printing blanket, the material incorporating the foaming agent is preferably applied to the stabilizing layer before the external pressure is applied and foaming is carried out. The face layer is preferably applied after the foaming procedure has been completed.

A hard stabilizing rubber layer having the characteristics previously described, is preferably applied to the foamed material before the face layer is applied and the face layer is applied over the hard rubber stabilizing layer.

It is generally a good idea to provide a good adhesive layer between the stabilizing substrate 11 and the foamed layer 15. The various layers may conveniently be applied by knife coating. Other methods of application, such as extrusion or calendaring, may also be used.

The method of printing according to the present invention involves the use of a closed celled foam disposed toward the printing indicia, preferably without any intervening fabric during printing. The closed celled foam is generally a virgin foam rubber free of any residue in the cells except of gas-producing blowing agent. The closed celled foam is preferably part of the printing element described above and has the properties already described.

While the present invention has been described with the principal purpose in mind, in particular that of producing a superior lithographic printing blanket in a very economical manner, it is obvious that the method lends itself to use in other foaming arts such as foaming polystyrene or polyurethane to obtain foams of greater strength than usually found and having special properties.

The term "super-atmospheric gas pressure" simply means a pressure deliberately elevated above the atmospheric pressure prevailing when the procedure is being carried out. "Plastic rubber" means a rubber that can flow. "Set" or vulcanized rubber is a rubber that upon stretching will recover to nearly its original shape in preference to flowing. "Foaming" means any method of forming bubbles or voids in a material by the expansion of gas or formation of gas within the material. "Compressible" means that the total volume of the material is reduced when the material is subjected to pressure.

The following Example further illustrates the present invention.

Example

A lithographic printing blanket was constructed in the following manner. The following ingredi nts were compounded in a Banbury mixer to form an expandable nitrile rubber compound.

INGREDIENTS	AMOUNT (PARTS)
Nitrile Rubber (HYCAR 1051—B. F. Goodrich)	100
Sulphur (Crystex 90—Stafford Chemical)	0.4
Blowing agent, heat activated, nitrogen releasing—p,p-oxybis-(benzene sulphonyl hydrazide) (Celogen OT—Uniroyal)	10
Dispersing Agent—aids in preventing cell collapse (VS-103 Airproducts & Chemical)	4
Dispersing Agent—stearic acid	1.5
Vulcanization activator—zinc oxide	5
Carbon Black N650 black	50
Anti-oxidant-symmetrical di-beta-naphthyl-p-phenylenediamine (Agerite white—R.T. Vanderbuilt)	1
Plasticizer—di(butoxy-ethoxy-ethyl) formal (TP-90B—Thiokol Chemical)	10
Accelerator—tetramethylthiuramdisulphide	3

All of the ingredients except the blowing agent, first listed dispersing agent and accelerator were initially mixed with a dump temperature of 275 to 290°F (135 to 143°C) and then those items were added with a maximum dump temperature of 185°F (85°C), lifting ram if necessary.

The expandable nitrile rubber mixture compounded above was dissolved in propylene dichloride solvent to form a 33% solution of the rubber compound by mechanical agitation. The solution had the approximate viscosity of molasses, viz. 120,000 cps as measured by a Brookfield Viscometer.

A backing substrate was positioned for knife coating with the solution of expandable nitrile rubber compound. The backing was a laminate of three layers of cotton fabric laminated together with neoprene adhesive and coated with a nitrile adhesive to provide good adhesion with the expandable nitrile rubber compound. The expandable nitrile rubber compound solution was knife coated over the nitrile adhesive to a thickness of 20 mils (0.5 mm). The solution was coated on in about 1/2 mil (0.0125 mm) thicknesses and the solvent removal was accelerated by heating to about 150°F (65°C) for about 60 seconds per pass through the coater until a 20 mil (0.5 mm) thickness was attained. Then talc was dusted on the surface to prevent the surface from being sticky.

A 37 yard (34 metre) length of the thus formed composite was placed in an autoclave in festoon fashion. The pressure in the autoclave was brought to 145 psi (10 kg/cm^2) gauge and the temperature was then raised to 285°F (140°C) over a period of about 4–5 minutes and then maintained for 8 minutes. The nitrile rubber compound was thereby foamed. After 8 minutes the pressure was released and the foamed composite structure was removed from the autoclave and cooled at ambient temperature. Then the face of the foamed nitrile rubber layer was ground with 240 grit abrasive paper to obtain an overall composite thickness of 59 mils (1.475 mm), with the fabric substrate making up approximately 41 mils (1.025 mm), the adhesive layer approximately 1 mil (0.025 mm) and the foamed nitrile rubber layer approximately 17 mils (0.425 mm).

The ground foamed surface was then knife coated with a 5 mil (0.125 mm) layer of the following hard rubber compound. The following ingredients were compounded in a Banbury mixer.

INGREDIENTS	AMOUNT (PARTS)
Nitrile Rubber (HYCAR 1051)	100
Thermosetting phenolic resin with 8% hexamethylenetetramine (Durez 12687—Dur z Plastic Divisi n of Hooker Chemical Co.)	55
Carbon Black N550	20
Precipitated hydrated silica HiSil 233—PPG Industries	20
Diethylene glycol	15
Zinc Oxide	5
Stearic Acid	2
Antioxidant-diphenylamine-acetone reaction product (Agerite-Superflex—R.T. Vanderbuilt)	2
Sulphur (Crystex 90)	0.5
n-(cyclohexylthio-phthalimide (Santogard PV1—Monsanto)	0.4

The thus formed compound was then dissolved in methyl ethyl ketone and toluene to form a 33% solution of the compound by mechanical agitation. A 10% solids solution in toluene of the following curing agents was prepared by mechanical agitation.

	AMOUNT (PARTS)
(2-morpholinothio) benzothiazole (Santocure MOR Monsanto)	1.23
Tetramethylthiuramdisulphide (Thiruad Monsanto)	0.8
Sulphur (Crystex 90)	0.6

The above two solutions were then combined and knife coated as already described. The hardness of the cured hard rubber was 85 durometer Shore A hardness.

A 5 mil (0.125 mm) thick layer of surface rubber was then knife coated over the hard rubber compound to provide an ink receptive transfer layer. The final thickness of the lithographic printing blanket is 67 mils (1.675 mm).

The void volume of the foam rubber layer was 31%; this was determined by immersing a small segment of the foam (.020 × 1 × 1 inch [0.05 × 2.5 × 2.5 cm]) in a solution of isopropanol and water of known density; the solution's density was measured by a calibrated hydrometer. By observing whether the sample floated or sank in a solution of known density it was determined whether the sample's density was less, if it floats, or greater, if it sinks. By adjusting the solution's density so that a floating sample just starts to sink the sample's density was estimated quite precisely. The density of the rubber before foaming was determined. Then using the density of the foamed and unfoamed rubber the void volume was calculated by the formula:

$$\%\text{ void volume} = \frac{\left(\dfrac{1}{\text{density of foam}} - \dfrac{1}{\text{density of rubber}}\right)}{\dfrac{1}{\text{density of foam}}} \, 100$$

$$31\%\text{ void volume} = \left|\frac{\left(\dfrac{1}{0.82} - \dfrac{1}{1.19}\right)}{\dfrac{1}{0.82}}\right| 100$$

The percentage of the closed cells was found to be approximately 95%. The average diameter was determined to be 4 to 5 mils (0.1 to 0.125 mm). Both of these last two parameters were

established as described above.

This lithographic printing blanket was then tested on a standard sheet feed lithographic press with good results.

Fig. 2 is a microphotograph of the lithographic printing blanket of Example 1. The adhesive layer penetrated into the yarn and thus the demarkation is not sharp but the adjacent foam cells are generally aligned in their lower extent thus showing fairly clearly that the adhesive has tended to serve a levelling function. The top foam cells are reasonably aligned showing the general margin between the hard rubber layer and the foamed high modulus rubber layer. The ink receptive transfer layer is the light coloured surface layer. The photomicrograph is on a scale of 1 inch = about 11 mils or a magnification of about 90.

CLAIMS

1. A resilient element suitable for use in printing comprising a base layer which is of a stabilizing material and an adhesive material, and a compressible layer which is a layer of foamed rubber having a substantially closed celled structure.

2. An element according to claim 1 comprising a hard rubber layer over the compressible layer opposite the base layer, no reinforcing fabric being present on the side of the compressible layer opposite said base layer.

3. An element according to claim 2 wherein said hard rubber layer has a Shore hardness A durometer reading of at least 75.

4. An element according to claim 2 or 3 comprising an ink receptive transfer layer over said hard rubber layer.

5. An element according to any one of claims 1 to 4 where at least 50% of the foamed cells are closed cells.

6. An element according to claim 5 wherein at least 80% of the foamed cells are closed cells.

7. An element according to any one of claims 1 to 6 wherein the closed cells have an average cell diameter of 0.0125 to 0.25 mm.

8. An element according to any one of claims 1 to 7 wherein said foam is a virgin blown foam formed by gas expansion and is substantially free of solid material within the closed cell walls of the rubber matrix other than blowing agent residue.

9. An element according to any one of claims 1 to 8 wherein said compressible layer has a void volume of at least 20%.

10. An element according to claim 9 wherein said compressible layer has a void volume of at least 30%.

11. An element according to any one of claims 1 to 10 wherein the compressible layer has a thickness of not more than 0.75 mm and is not more than 0.5 mm from the outer surface of said element opposite said base element.

12. An element according to claim 11 wherein the compressible layer has a thickness of not more than 0.5 mm and is not more than 0.375 mm from the face of said element.

13. An element according to claim 1, substantially as described in the Example.

14. A method of printing comprising absorbing the printing forces in the printing nip with a closed cell foam element.

15. A method according to claim 14 wherein said closed celled foam is disposed toward the printing indicia without any intervening fabric.

16. A method according to claim 14 or 15 wherein a hard rubber layer is disposed between the printing indicia and the closed celled foam element.

17. A method according to any one of claims 14 to 16 wherein said hard rubber layer has a Shore hardness A durometer reading of at least 75.

18. A method according to any one of claims 14 to 17 wherein said closed celled foam element possesses one or more of the features of claims 5 to 10.

19. A method according to any one of claims 14 to 18 wherein the closed celled foam element is not more than 0.875 mm from the printing indicia.

20. A method according to any one of claims 14 to 19 wherein the closed cell foam element is one claimed in any one of claims 1 to 13.

21. A process for foaming a material comprising incorporating a foaming agent in said material, if said material does not already contain a foaming agent, and foaming said material while subjecting the material to an external pressure that yields to said foaming while remaining intact.

22. A process according to claim 21 wherein said external pressure on the material during foaming is at least 0.7 kg/cm² gauge.

23. A process according to claim 21 or 22 wherein said material is a plastic rubber when said foaming begins and is a significantly set rubber before said foaming is complete.

24. A process according to claim 23 wherein said rubber is applied to a stabilizing layer

layer.

25. A process according to claim 24 wherein a hard rubber layer having a Shore hardness A durometer reading of at l ast 75 is provided between the foamed layer and the face layer and no reinforcing fabric is present between said foamed layer and said fac lay r.

26. A process according to any one of claims 21 to 25 wherein said rubber is foamed to provid a layer possessing one or more of the features of claims 5 to 10.

27. A process for foaming a material having an internal foaming agent comprising applying super-atmospheric gas pressure to the outer surface of said material, heat activating said foaming agent while maintaining said super-atmospheric gas pressure on the outer surface of said material thereby to foam said material while maintaining said super-atmospheric gas pressure on the outer surface of said material.

28. A process according to claim 27 having one or more of the features of claims 22 to 26.

29. A process according to claim 27 or 28 wherein said external gas is air and said gas pressure is 3.5 to 14 kg/cm^2 gauge.

30. A process according to any one of claims 27 to 29 wherein the setting of said rubber is by vulcanization.

31. A process according to any one of claims 27 to 30 wherein said material incorporating said foaming agent is applied to a stabilizing layer before said gas pressure is applied and after said foaming a face layer is applied over the foamed material opposite said stabilizing layer.

32. A process according to claim 21 or 27, substantially as described in the Example.

33. A material whenever foamed by a process as claimed in any one of claims 21 to 31.

34. A lithographic printing blanket whenever prepared by a process as claimed in any one of claims 24 to 26, 28 and 31.

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